Cocoa Beach 05

Synthesis of Boron Nitride Nanotubes for Engineering Applications

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Boron Nitride nanotubes (BNNT) are of interest to the scientific and technical communities for many of the same reasons that carbon nanotubes (CNT) have attracted large amounts of attention. Both materials have potentially unique and significant properties which may have important structural and electronic applications in the future. However of even more interest than their similarities may be the differences between carbon and boron nanotubes. While boron nitride nanotubes possess a very high modulus similar to CNT, they are also more chemically and thermally inert. Additionally BNNT possess more uniform electronic properties, having a uniform band gap of ~ 5.5 eV while CNT vary from semi-conducting to conductor behavior.

Boron Nitride nanotubes have been synthesized by a variety of methods such as chemical vapor deposition, arc discharge and reactive milling. Consistently producing a reliable product has proven difficult. Progress in synthesis of 1-2 gram sized batches of Boron Nitride nanotubes will be discussed as well as potential uses for this unique material.

SYNTHESIS OF BORON NITRIDE NANOTUBES FOR ENGINEERINGING APPLICATIONS

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NASA's Long Term Nanotube Interests

- Thread –CNT in long lengths – could replace nylon and other fibers for spacesuits, ropes, webbings, life support tethers, inflatable habitats, orbital debris shields
- Electrostatic Discharge Materials- dissipate static charge in computer screens
- Life Support Systems and Nanosensors- Lighter and stronger oxygen tanks, gas adsorption of toxic gases such as NO_2, NO, etc. which accumulate over time, substrates for catalytic conversion of NO_x to N_2 and O_2, sensors for NO_x
- Biomedical
- Composites – mechanically strong, light weight
- Nanoelectronics – ultra small and ultra fast computing
- Energy Storage – batteries, ultracapacitors, fuel cells
- Thermal Materials – CNT will burn in air, but may be useful for intermediate temperatures. BNNT is suitable for very high temperatures

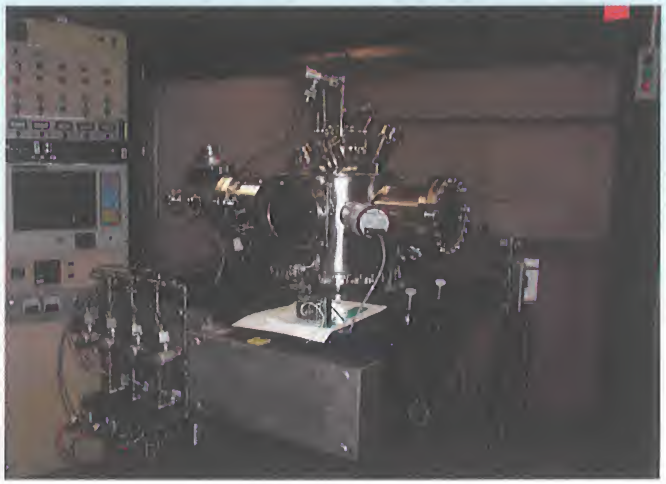
NASA GRC Ceramic Branch Objective

- Develop and optimize synthesis techniques to create BN nanotubes in sufficient quantities for evaluation of potential applications. Applications of interest to NASA include:

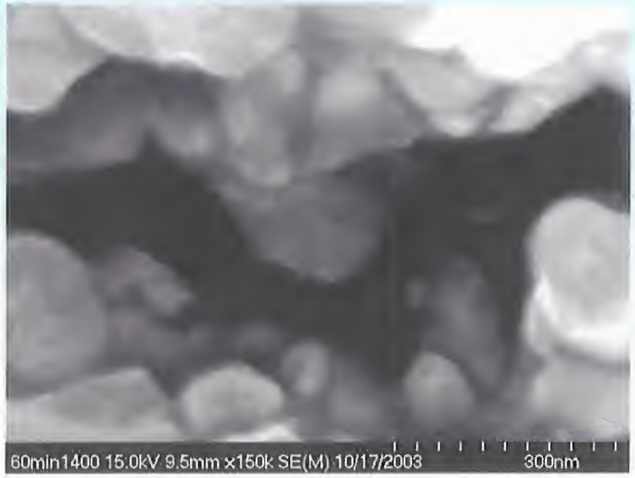
  1. high temperature electronics and sensor components for intelligent engines,
  2. miniaturization of electronics and sensors
  3. reinforcement of light weight and/or ceramic matrix composites
  4. hydrogen storage media for fuel cell applications.

Current effort is divided into -

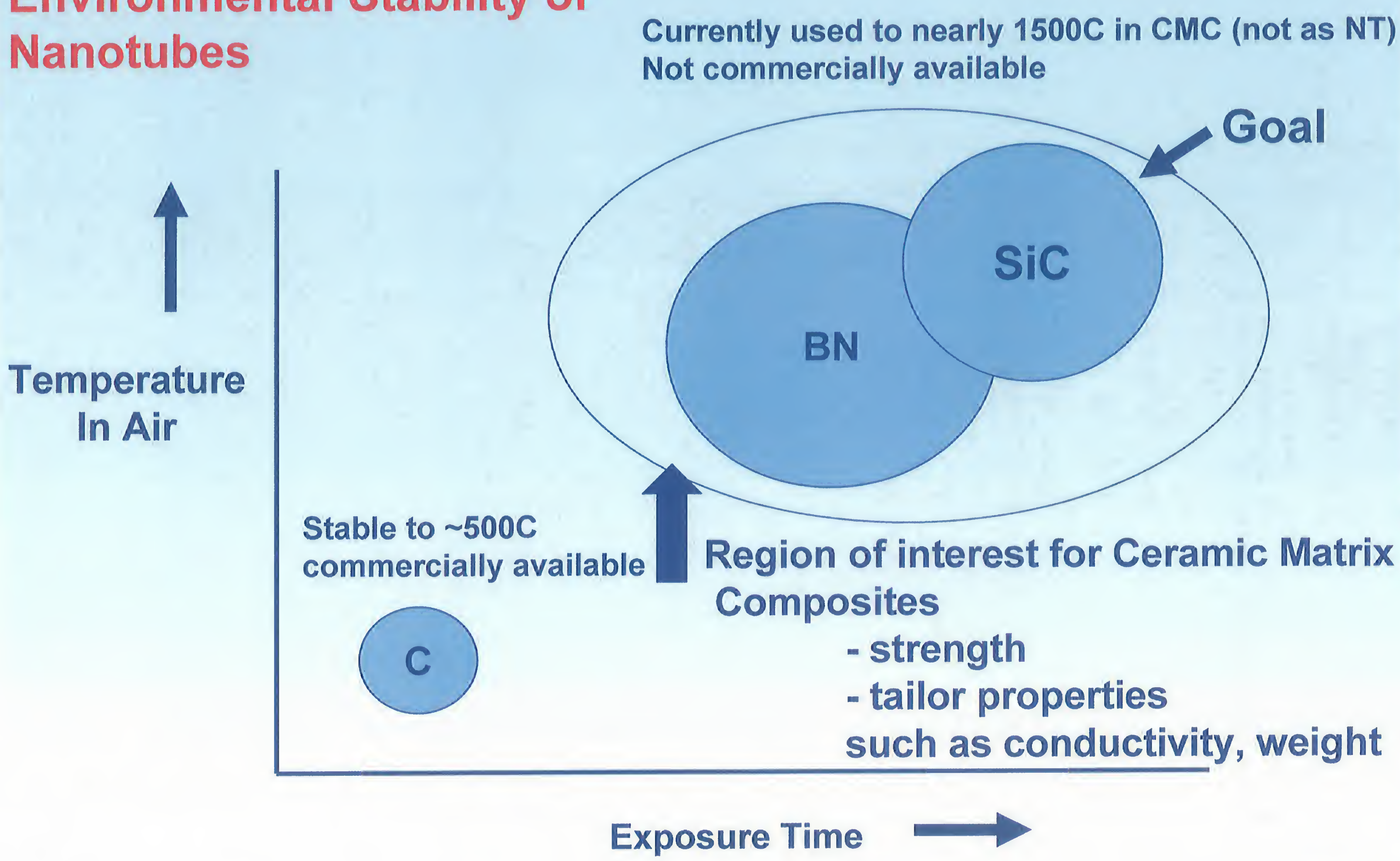
1. Synthesis of BN Nanotubes for H2 Storage, Composites, Energy Storage



2. Nanotube Reinforced Ceramic Matrix Composites for Structural Applications



Environmental Stability of Nanotubes



Why BN Nanotubes?

Forms graphene sheets - similar to carbon

Excellent mechanical properties, light and flexible, nearly as strong as CNT (Zhang and Crespi, PRB 2000) – modulus is 93% of CNT (1 TPa) – potential structural applications

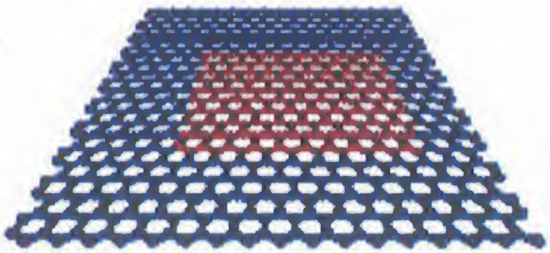
Very oxidation resistant - currently used in state-of-the-art high temperature composites to 2700F (~1500C) – replacement for C as interfacial coating due to carbon's poor oxidation resistance – compatible with current processing techniques

Chemically inert – suitable for coatings, high temperature applications

Consistent insulator – constant band gap of ~5eV, whereas CNT varies from semi-conducting to metallic depending on chirality's and diameters

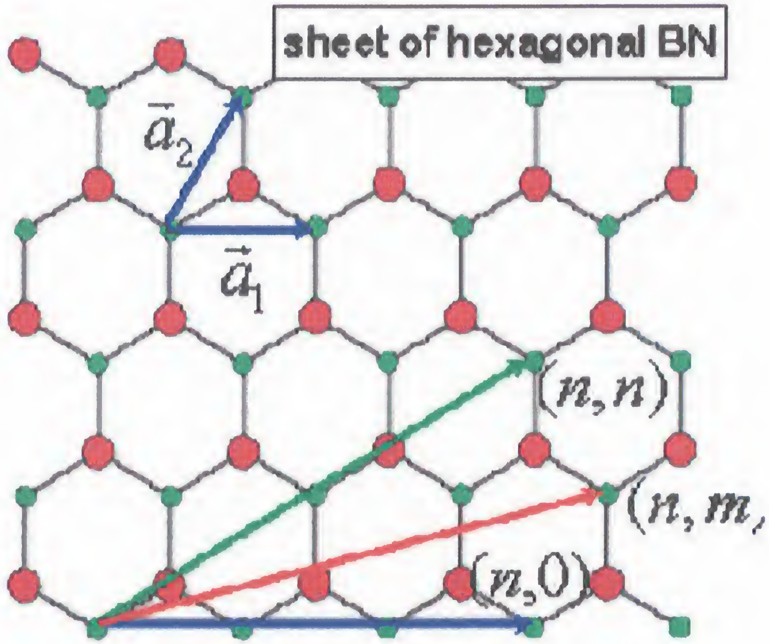
Intrinsically polar – polar B-N bond – potential applications as piezoelectric sensors, Nano-Electric-Mechanical Systems (NEMS), field effect devices and emitters

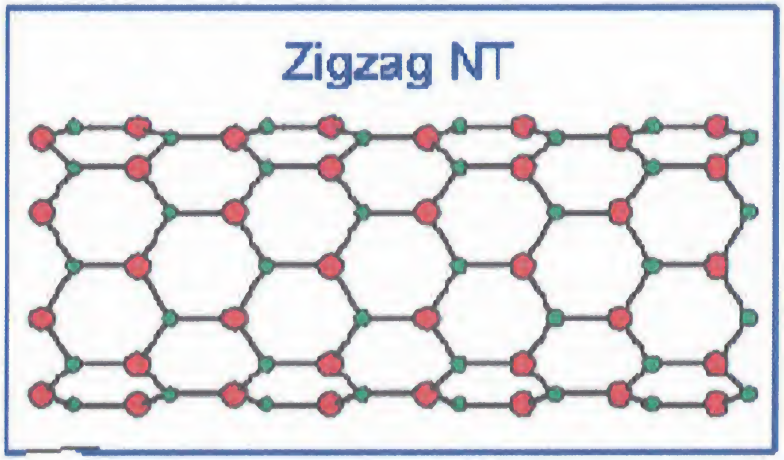
Hydrogen storage – bamboo structure can theoretically store up to 18 w/0 - fuel cell applications



"Zigzag"

"Armchair"





BN preferentially forms Zigzag NT

N. Carolina State

NASA Rapid Processing Method

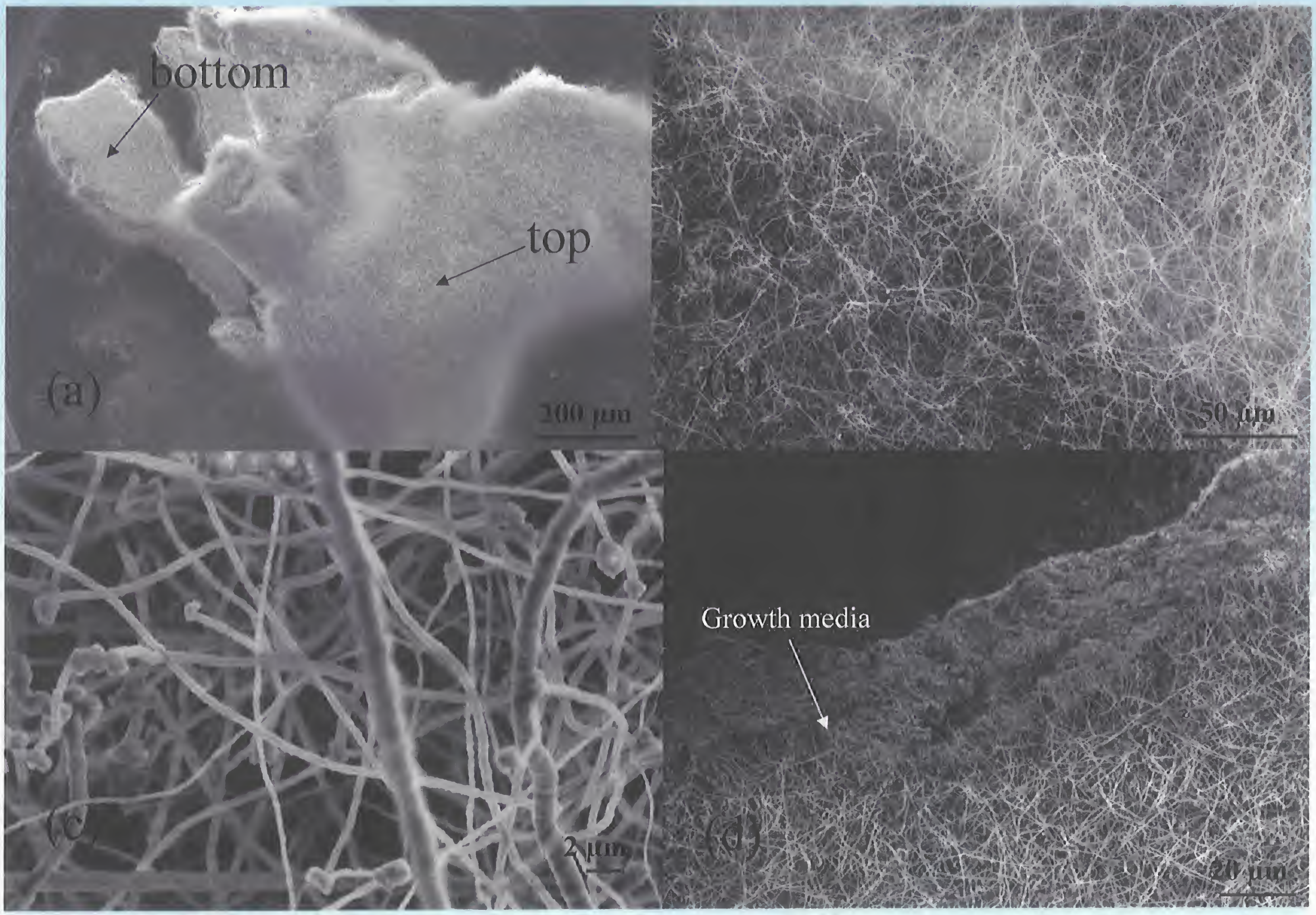
Features-

- Easy production
- High yield
- Short processing time (hours)
- Very reproducible
- Insitu production of nanotubes on surfaces and preforms

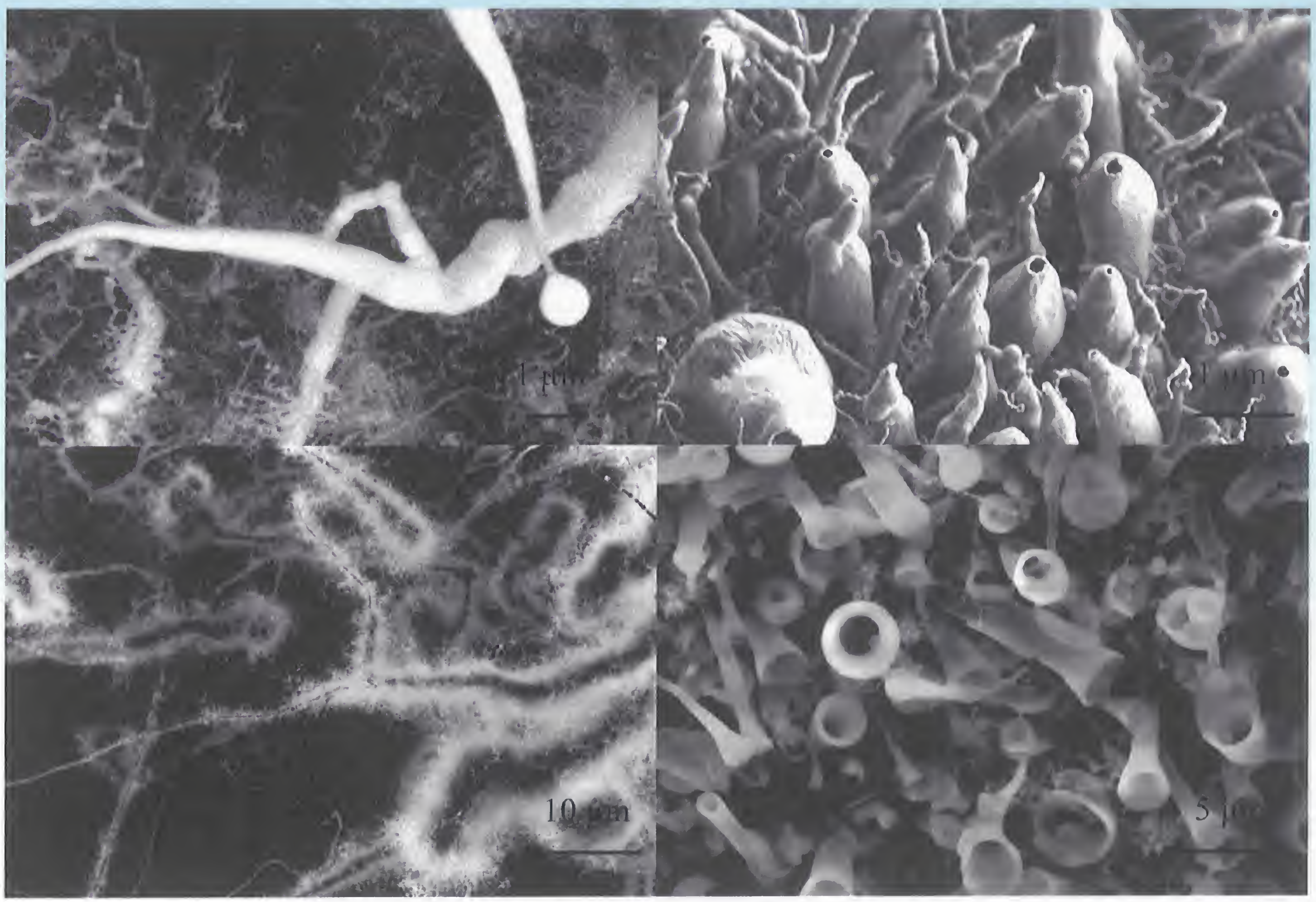
Description - A Boron containing material mixed with catalysts is heated under a flowing nitrogen/ammonia gas mixture to 1350C.

Field emission scanning electron microscope images of BNNT

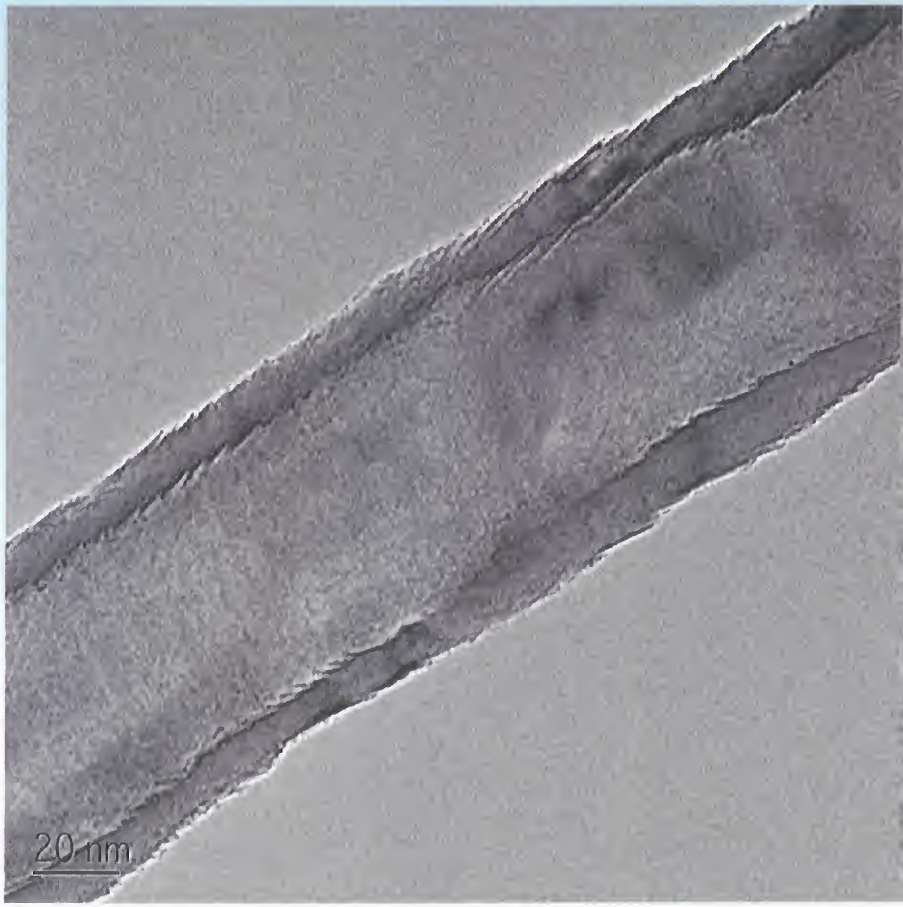
(a) Typical flake peeled from substrate. (b)(c) Higher magnification photos of typical areas. (d) BNNT growing from media.

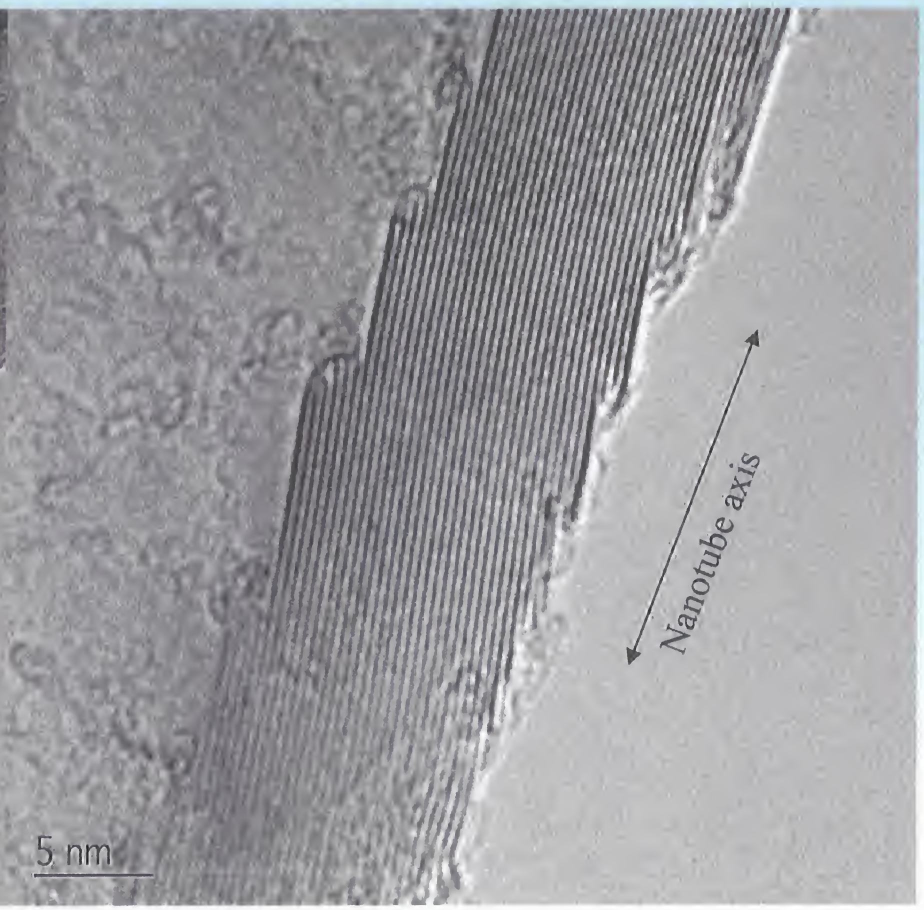


Examples of less typical structures synthesized at processing extremes.
a) Adjacent extremes in size. b) open ended nanopods
c) fine BNNT nucleated on larger tubes
d) nanohorns.

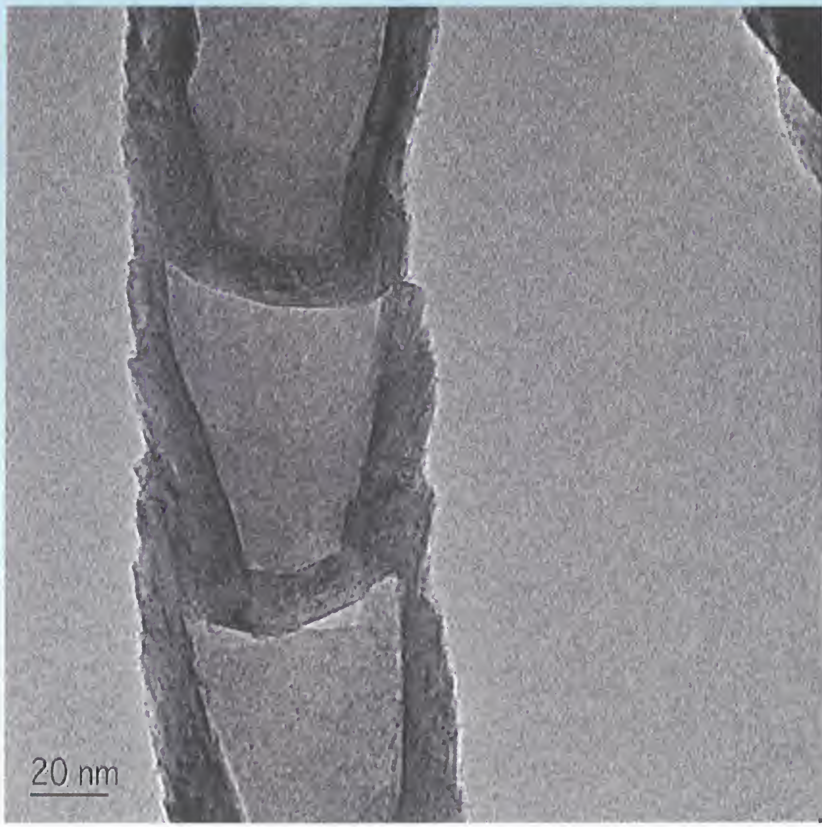


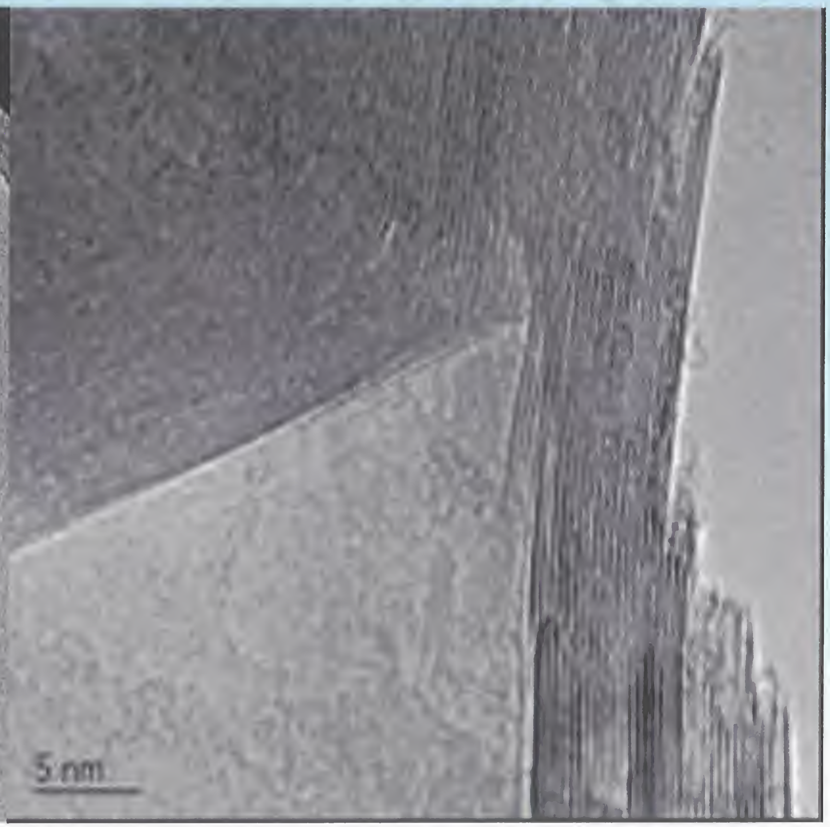
TEM photos of typical straight walled BNNT



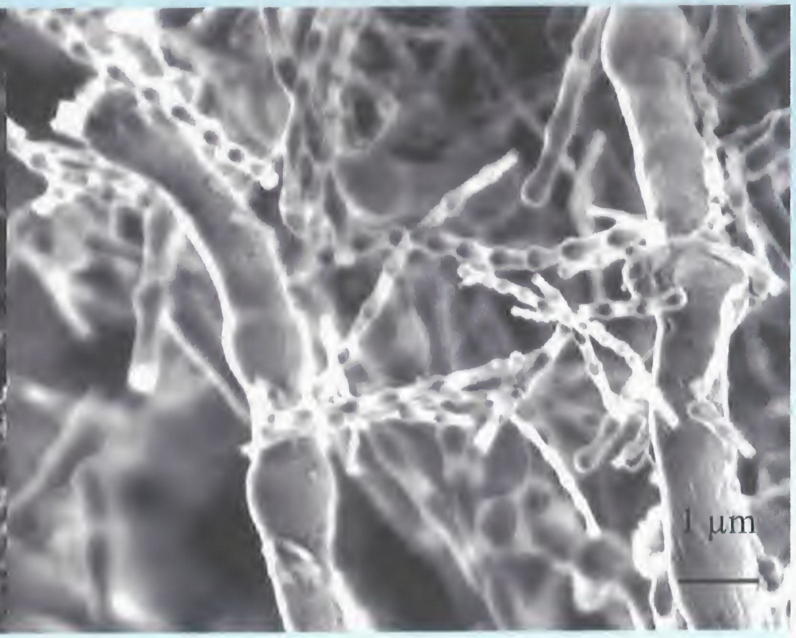


TEM photos of typical bamboo BNNT

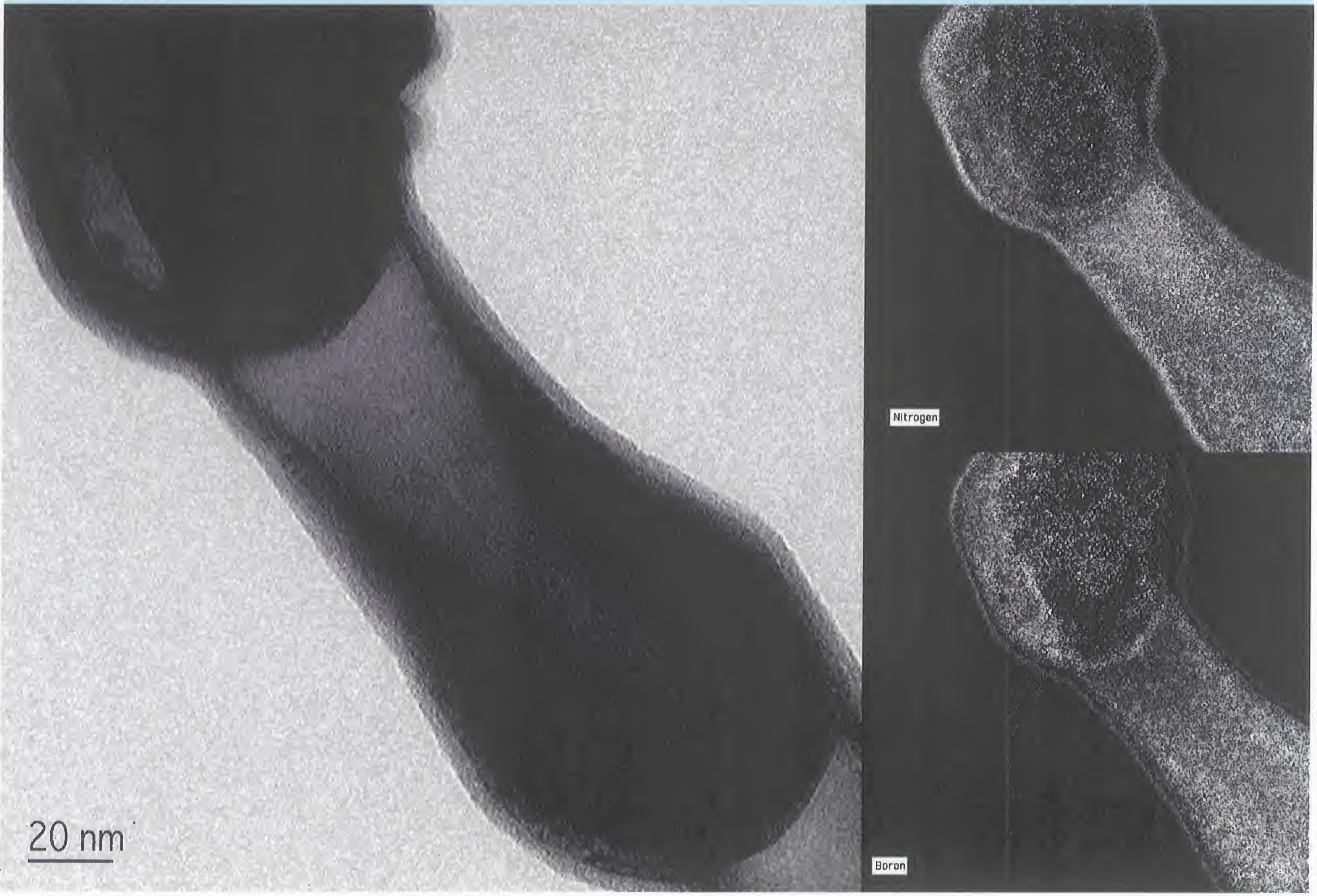




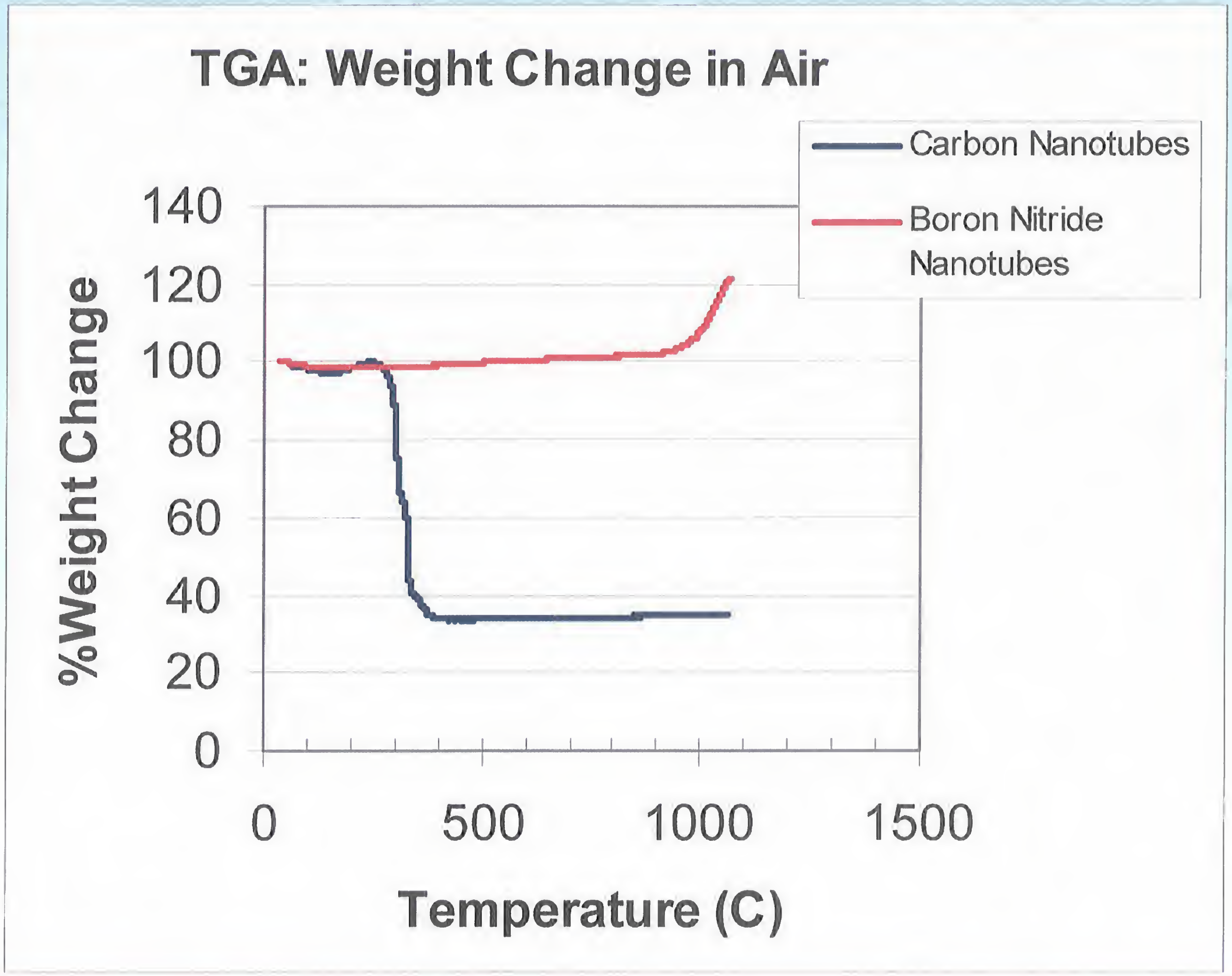
Regions of predominately bamboo nanotubes structures



Growth Tip of Bamboo Nanotube

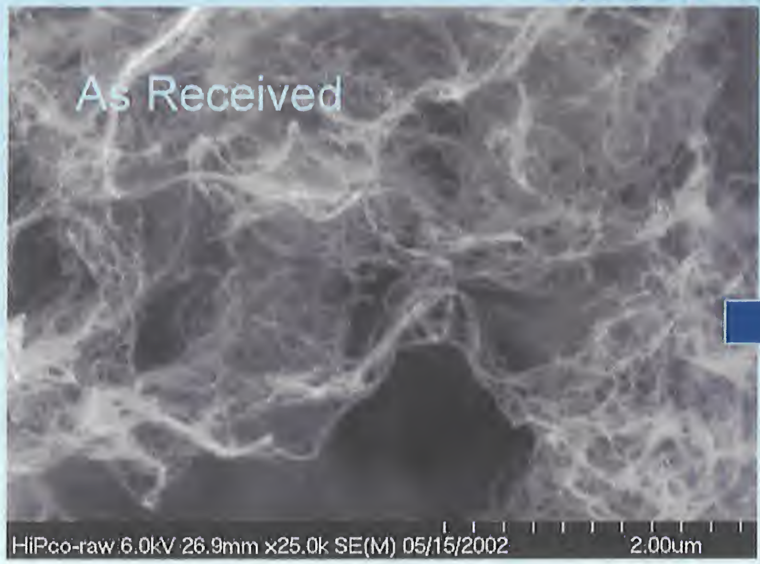


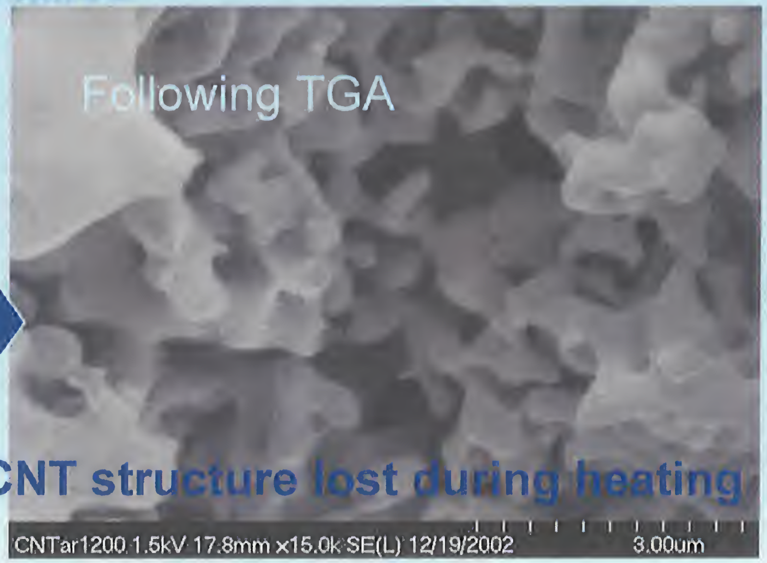
BN Nanotubes Provide Far Greater Temperature Stability Relative to Carbon Nanotubes



BN Nanotubes Retain Structure Following Heating to 1000C in Air

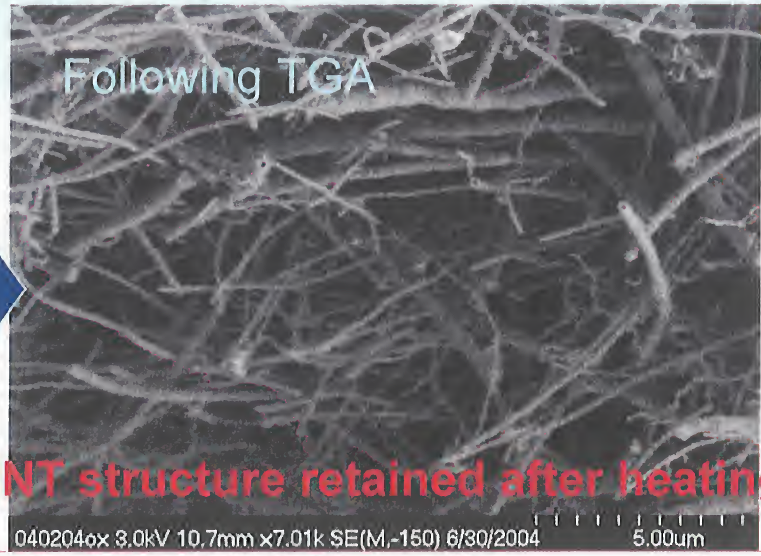
Carbon nanotubes -





CNT structure lost during heating

BN nanotubes -



BNNT structure retained after heating

Engineering Benefits - Potential New Missions to Meet Agency Goals

Super nano capacitors – *LEAP, AEFT, Code T*

- Energy storage for device power management - coupling super capacitors with fuel cells offers a system with the ability to deliver pulses of peak power
- Used in conjunction with fuel cells, super caps can operate at high/low temps, can't explode, are lightweight, can charge/discharge over a million times, nontoxic.

Fuel Cells – *LEAP, AEFT*

- High energy storage density - hydrogen storage media for fuel cells and hydrogen propulsion - theoretically BN nanotubes can store up to 17 weight percent hydrogen, far in excess of the DOE goal of 6.5 weight percent
- Reinforcement for seals for SOFC – 800 C seal temperature is too hot for CNT or carbon fibers
- "Nanotube Fuel Cell Developed for Pacific Fuel" – Smalltimes, MWCNT based electrodes in proton exchange membrane

Nano Transistors – *intelligent engine applications, robotics*

- BNNT is a semiconductor, excellent for high temperature applications where CNTs would burn - could revolutionize electronics

Piezoelectrics – *intelligent engine applications, robotics*

- Theoretically BNNT has piezo properties, could be *high temperature sensors AND structural reinforcement – multifunctional devices*

Structural – *Code R, LEAP*

- weight reduction, reinforcement

NASA Rapid Processing Method for BN Nanotube Synthesis on Substrates

- Reduced processing times from one batch per month to one batch daily
- Improved reproducibility found for BN nanotube batches
- Can grow BN nanotubes in-situ on other materials as a substrate – can grow BN nanotubes on SiC fiber as an example. Possible CMC and EBC application

As-produced Rapidly Processed BN Nanotubes on Substrates

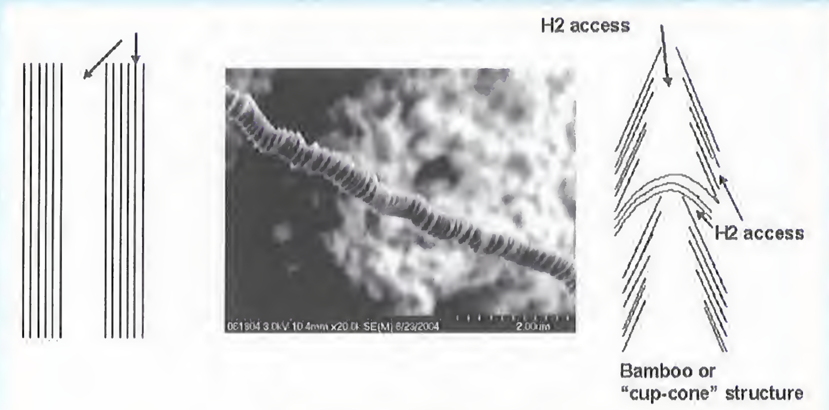
- BN nanotubes shown above were synthesized in-situ on the surface of a SiC fiber within a fiber preform (preform is composed of Sylramic fiber).

Unique Structure of BN Nanotubes (BNNT) Ideal for Hydrogen Storage

Cup-cone structure – allows easy access to interior for hydrogen storage

(carbon NT may require "chopping" as hydrogen does not travel through center of tube)

Preferred BNNT structure



Closed ends of BNNT can be easily opened by a thermal treatment at 800 C - However carbon NT can not survive this temperature – but BNNT can. Open ends are necessary for hydrogen storage

Photos of NASA Glenn Synthesized BN Nanotubes

BN Prototype Capacitors

Conclusions

- The NASA rapid processing method was the most promising in terms of maximizing batch size and percentage yield. Batch sizes of 1-2 g have been successfully prepared.

- The temperature stability of BN nanotubes in air is significantly higher than that for commercially available carbon nanotubes. The carbon nanotubes lose weight rapidly at 400 °C as the carbon is oxidized.

- Insitu production BN nanotubes inside ceramic SiC preforms and other substrates was successfully demonstrated.

Future Work

BN reinforced ceramic composites

- glass composite for solid oxide fuel cell seals

Separation of BNNT from BN nanoparticles

Continued evaluation of BN nanotubes for hydrogen storage

Ultra Capacitors

Electronics

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